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## (54) PRODUCTION OF HIGH TENSILE STRENGTH HOT DIP GALVANIZED STEEL SHEET AND HOT DIP GALVANNEALED STEEL SHEET

### (57)Abstract:

PROBLEM TO BE SOLVED: To impart an excellent appearance free from unplating to a steel sheet by subjecting a steel sheet contg. specified amounts of Si, Mn and Cr to oxidation treatment and reduction at specified temp. for a specified time, moreover specifying the relation between the oxidizing time and reducing time and next executing hot dip galvanizing.

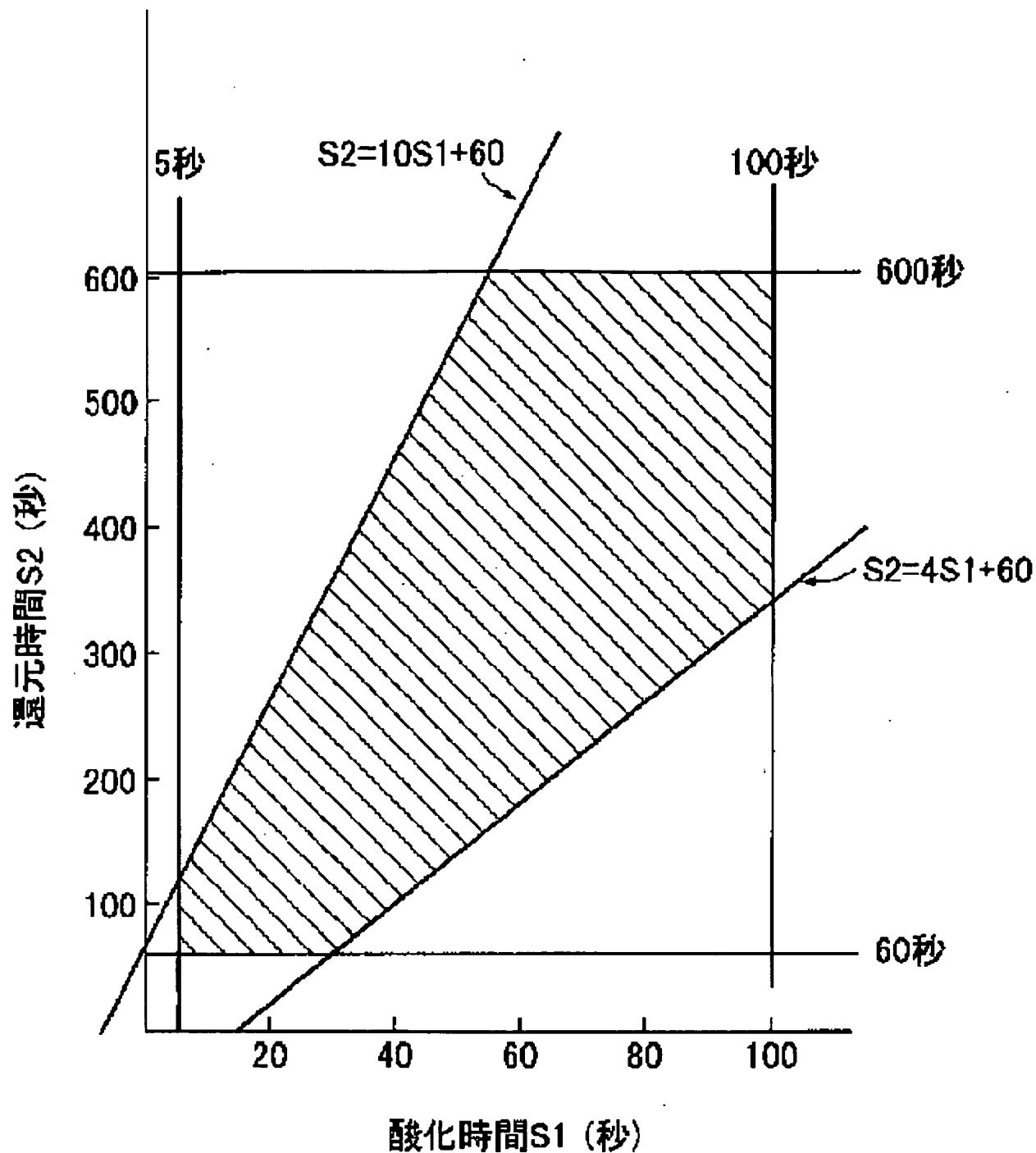
SOLUTION: Steel contg., by mass, 0.1 to 2% Si, 0.5 to 3% Mn and  $\leq$ 1% Cr (including 0%), and in which the total content of Si, Mn and Cr is also controlled to 0.6 to 5% is subjected to oxidation treatment at 200 to 650°C for 5 to 100 sec and is next subjected to reduction at 600 to 650°C for 60 to 600 sec in an annealing furnace. At this time, the oxidizing time (S1) (sec) and the reducing time (S2) (sec) are allowed to satisfy the relation in the inequality of  $4 \times (S1) - 60 \leq (S2) \leq 10 \times (S1) + 60$  to suppress the surface concn. of the elements to be added at the time of the annealing. Next, the steel sheet is applied with hot dip galvanizing and is, if required, subjected to alloying treatment.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] Si: 0.1-2% (it is the same the semantics of mass %, and the following), Mn:0.5-3%, Contain less than [ Cr:1% ] (0% is included), respectively, and it faces manufacturing a hot-dip zinc-coated carbon steel sheet using the steel plate whose sum total content of Si, Mn, and Cr is 0.6 - 5%. A steel plate is oxidized for 5 to 100 seconds at 200-650 degrees C. With the afterbaking annealing furnace The manufacture approach of the high tension hot-dip zinc-coated carbon steel sheet which decides to return for 60 to 600 seconds at 600-900 degrees C, and is characterized by satisfying the relation of following the (1) type about oxidation time amount (S1) (second) and reduction time amount (S2) (second) in this case, and giving hot dip zining succeedingly.

$$4x(S1)-60 \leq (S2) \leq 10x(S1)+60 \dots (1)$$

[Claim 2] The manufacture approach of the alloying galvanized steel sheet which alloys the plating layer of the hot-dip zinc-coated carbon steel sheet obtained by the approach of claim 1, and is used as an alloying hot-dip zinc-coated carbon steel sheet.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the approach of manufacturing the various plating steel plates which present the good surface appearance which raises the plating nature of the steel plate which added Si, Mn, and Cr especially about the useful approach for manufacturing the high tension hot-dip zinc-coated carbon steel sheet used for the rust-proofing steel plate for automobiles, the alloying hot-dip zinc-coated carbon steel sheet which alloyed the plating layer of such a hot-dip zinc-coated carbon steel sheet, and does not have a non-galvanized part.

#### [0002]

[Description of the Prior Art] In recent years, the lightweight-ized needs of an automobile are increasing for the purpose of global warming prevention, and high tension-ization of a material is strongly demanded from safety and a viewpoint of lightweight-izing. Although Si and Mn are added by the steel plate and Cr is added by the need from a viewpoint of on the other hand obtaining a high-tensile-steel plate with good workability, the steel plate which added these elements has the problem that plating nature deteriorates. That is, since elements, such as Si, Mn, and Cr, are called easy-oxidizable element, they oxidize preferentially in a reducing atmosphere and condense on a steel plate front face; and this will degrade plating wettability remarkably, will generate the so-called non-galvanized part, and will spoil a plating appearance.

[0003] In order to solve the above problems, the plating layer which techniques various until now are proposed, for example, becomes JP,57-70268,A, JP,2-156056,A, and 4-333552 from one sort of metals, such as Fe, nickel, and Co, or two sorts or more to the steel plate before hot-dip-zincing processing is pre galvanized, and the approach of controlling steel plate surface concentration, such as Si, Mn, Cr, etc. which oxidize preferentially by the reducing atmosphere, is indicated.

[0004] Moreover, by controlling the excess air ratio of combustion gas, the inside of a direct heating furnace is made into an oxidizing atmosphere, and the approaches (for example, JP,55-122865,A, JP,4-276057,A, JP,6-81096,A, etc.) of making generate the oxide film of Fe preferentially and controlling steel plate surface concentration in a reducing furnace, such as Si, Mn, and Cr, are also learned for the hot-dip-zincing facility which has a clean-heating-furnace (NOF) type annealing furnace.

#### [0005]

[Problem(s) to be Solved by the Invention] By the way, in a continuation hot-dip-zincing facility equipped with the annealing furnace (vertical-type annealing furnace) of an indirect heating method, since electroplating is generally used by the pre galvanizing method in order to apply the above conventional techniques to this appearance in hot-dipping Rhine, there is a problem that plant-and-equipment investment expense becomes high, and a manufacturing cost also becomes high again.

[0006] On the other hand, although the excess air ratio of a burner is controlled by the oxidation reduction process by the NOF type annealing furnace and the oxide film of proper iron is fundamentally generated with

it, since the amount of oxygen of a minute amount is adjusted, there is another problem that adjustment of each burner becomes difficult, the amount of oxygen becomes unstable and generation of the amount of oxygen coats also becomes unstable as a result.

[0007] This invention is made under such a situation, and even if the continuation hot-dip-zincing facility which has the annealing furnace of an indirect heating method is used for the purpose, it is to offer the useful approach for manufacturing a hot-dip zinc-coated carbon steel sheet and an alloying hot-dip zinc-coated carbon steel sheet which un-galvanizing does not produce.

[0008]

[Means for Solving the Problem] With the manufacture approach of this invention that the above-mentioned purpose could be attained Si:0.1-2% and Mn:0.5-3%, contain less than [ Cr:1% ] (0% is included), respectively, and it faces manufacturing a hot-dip zinc-coated carbon steel sheet using the steel plate whose sum total content of Si, Mn, and Cr is 0.6 - 5%. A steel plate is oxidized for 5 to 100 seconds at 200-650 degrees C. With the afterbaking annealing furnace It supposes that it returns for 60 to 600 seconds at 600-900 degrees C, the relation of following the (1) type is satisfied about oxidation time amount (S1) (second) and reduction time amount (S2) (second) in this case, and it has a summary at the point of giving hot dip zinching succeedingly.

$$4x(S1)-60 \leq (S2) \leq 10x(S1)+60 \dots (1)$$

Moreover, the good alloying hot-dip zinc-coated carbon steel sheet of a property without a non-galvanized part can be obtained by alloying the plating layer of the hot-dip zinc-coated carbon steel sheet obtained by the above approaches.

[0009]

[Embodiment of the Invention] if Si, Mn, and Cr return directly the steel plate which carries out specified quantity content with the annealing furnace (indirect heating type annealing furnace) with which the continuation hot-dip-zincing facility is equipped -- like the above-mentioned -- a steel plate front face -- the front face of these components -- concentration will arise and a non-galvanized part will occur. after [ then, ] this invention persons made the steel plate front face generate an iron oxide film stably -- reduction annealing -- carrying out -- the front face of an alloying element -- it examined preventing concentration.

[0010] consequently -- if it becomes clear that the oxidation conditions performed before introducing into a reduction annealing furnace, and the reduction conditions kicked to a reduction annealing furnace are influenced by whenever [ each board temperature ], and time amount, whenever [ these board-temperature ], and time amount are controlled appropriately and oxidation conditions and reduction conditions are specified -- the front face of an alloying element -- a header and this invention were completed for being able to prevent concentration and the above-mentioned purpose being attained splendidly. Hereafter, each requirement specified by the manufacture approach of this invention is explained.

[0011] Although a steel plate is oxidized at 200-650 degrees C before introducing this invention approach into an annealing furnace, however there may be too many amounts of generation of an oxide film when the temperature at this time (whenever [ board temperature ]) does not fully generate at less than 200 degrees C and an oxide film exceeds 650 degrees C, and it may set up that condition in the reduction processing by the usual reduction annealing furnace, a non-galvanized part will occur by survival of an iron oxide film.

[0012] Oxidation treatment by the above-mentioned oxidation temperature needs to make the time amount 5 - 100 seconds. When this oxidation time amount of generation of an iron oxide film is insufficient and exceeds 100 seconds in less than 5 seconds, there will be too many amounts of generation of an oxide film, and they will produce the same phenomenon as the above. In addition, especially about the heating method for oxidation treatment, it cannot limit and both indirect heating induction heating direct fire heating and energization heating can be adopted. Moreover, although the ambient atmosphere at this time has the most common inside of atmospheric air, what is necessary is just an oxidizing atmosphere equivalent to this.

[0013] On the other hand, it is necessary to make temperature in the case of reduction processing (whenever

[ board temperature ]) into 600-950 degrees C. Sufficient reduction cannot be performed with this temperature being less than 600 degrees C, but an iron oxide film will remain, and a non-galvanized part will occur. Moreover, when reduced temperature exceeds 950 degrees C, reduction will progress quickly, an iron oxide film will be returned in the state of an elevated temperature, and concentration of an alloying element will occur. The temperature in the case of the reduction processing from such a thing was specified as 600-950 degrees C.

[0014] The reduction processing by the above-mentioned reduced temperature needs to make the time amount 60 - 600 seconds. When it becomes insufficient in less than 60 seconds returning this reduction time amount and it exceeds 600 seconds, returning becomes superfluous and the same un-arranging it as the above will arise.

[0015] Although oxidation treatment and reduction processing are performed on the above oxidation conditions (whenever [ board temperature ] - time amount) and reduction conditions (whenever [ board temperature ] - time amount), in order to attain the purpose of this invention, it is necessary by this invention approach to also control appropriately the relation between the oxidation time amount at this time (S1), and reduction time amount (S2). That is, the above-mentioned oxidation time amount (S1) and reduction time amount (S2) need to be satisfied with this invention approach of the relation of following the (1) type.

$$4x(S1)-60 \leq (S2) \leq 10x(S1)+60 \dots (1)$$

[0016] The range of the oxidation time amount (S1) specified by this invention and reduction time amount (S2) including the range specified by the above-mentioned (1) formula is shown in drawing 1. That is, as it is within limits shown by hatching of drawing 1, after controlling oxidation time amount (S1) and reduction time amount (S2), the hot-dip zinc-coated carbon steel sheet and alloying hot-dip zinc-coated carbon steel sheet which prevent non-galvanized generating and have a good surface appearance were able to be manufactured by performing hot dip zining and performing alloying processing as occasion demands. That is, when it separates from the range shown by hatching of drawing 1, all will generate un-galvanizing.

[0017] In the continuation hot-dip-zincing facility equipped with the indirect heating type annealing furnace by this invention as mentioned above By controlling appropriately the oxidation conditions at that time, and subsequent reduction conditions, making an iron oxide film form in a steel plate front face, before introducing into a reduction annealing furnace the front face of elements, such as Si, Mn, Cr, etc. which generate un-galvanizing, -- it was able to control generating, before concentration galvanizing and the good surface appearance without un-galvanizing was able to be acquired.

[0018] however -- if each content of Si, Mn, and Cr in a steel plate has exceeded the range of predetermined in these sum total contents in the list even if it specifies oxidation conditions and reduction conditions as mentioned above -- the front face of these elements -- concentration cannot be controlled. Moreover, although the problem that it does not galvanize will not be generated by processing by the usual annealing furnace, either, if Mn has not added [ Si in a steel plate ] Cr less than 0.5% less than 0.1% (impurity level) and the sum total content of these elements becomes less than 0.6%, it becomes difficult to attain tension strength (for example, 340 or more MPas) required as high tensile steel. From such a thing, less than [ Cr:1% ] (0% is included) and the sum total content of Si, Mn, and Cr were specified for the content of the above-mentioned element in the base steel plate used by this invention as 0.6 - 5% Si:0.1-2% and Mn:0.5-3%.

[0019] In addition, although various elements, such as Ti, Nb, Mo, V, Zr, N, and B, are contained in the steel plate used by this invention by the need besides fundamental components, such as C, aluminum, P, and S, as components other than Above Si and Mn and Cr, what is necessary is just extent which does not limit especially about these contents and is usually contained as a base steel plate. Moreover, the minor constituent of extent which does not affect the property may also be included in the steel plate used by this invention besides these, and it is contained in the base steel plate which also uses such a steel plate by this invention.

[0020] Hereafter, although an example explains this invention to a detail further, the following example is not the thing of the property which limits this invention, and each thing marked and done to before and the after-

mentioned meaning for a design change is included in the technical range of this invention.

[0021]

[Example] After performing oxidation treatment in atmospheric air using the various steel plates included as Si, Mn, and Cr were shown in the following table 1, reduction processing was performed with the indirect heating type annealing furnace. Subsequently, about the steel plate which performed these processings, eye melting zinc reached on condition that usual, and alloying processing was performed. Plating nature was investigated about the obtained alloying hot dip zining. About the plating nature at this time, it observed visually, and evaluated as x about that in which O and un-galvanizing generated the thing of a good appearance without un-galvanizing. These results are shown in the following table 1 with oxidation-treatment conditions and reduction processing conditions.

[0022]

[Table 1]

No.	鋼中添加元素(質量%)				酸化条件		還元条件		(1)式で規定されるS2の範囲	めつき性	備考
	Si	Mn	Cr	合計	板温(°C)	時間(秒)	板温(°C)	時間(秒)			
1	0.2	1.5	—	1.7	250	20	800	240	20~260	◎	実施例
2	0.2	2.5	0.5	3.2	300	15	850	120	0~210	◎	実施例
3	0.4	1.5	0.2	2.1	640	30	900	280	60~360	◎	実施例
4	1.0	2.0	0.3	3.3	430	45	750	220	120~510	◎	実施例
5	1.8	2.5	0.4	4.7	650	60	880	650	180~660	◎	実施例
6	0.2	1.5	—	1.7	480	90	650	580	300~960	◎	実施例
7	0.2	2.5	1.0	3.2	220	75	700	590	240~810	◎	実施例
8	0.4	1.5	0.2	2.1	380	30	750	140	60~360	◎	実施例
9	1.0	2.0	0.3	3.3	450	10	820	80	-20~160	◎	実施例
10	1.8	2.5	0.4	4.7	480	25	830	280	40~310	◎	実施例
11	2.5	1.0	0.2	3.7	380	30	750	140	60~360	×	比較例
12	2.0	3.0	0.5	5.5	550	60	880	550	180~660	×	比較例
13	0.2	1.5	—	1.7	480	3	650	100	-40~110	×	比較例
14	0.2	2.5	0.5	3.2	220	75	700	650	240~810	×	比較例
15	0.4	1.5	0.2	2.1	180	30	750	140	60~360	×	比較例
16	1.0	2.0	0.3	3.3	450	10	980	80	-20~160	×	比較例
17	1.8	2.5	0.4	4.7	480	25	830	60	40~310	×	比較例
18	0.4	1.5	0.2	2.1	700	30	750	140	60~360	×	比較例
19	0.4	1.5	0.2	2.1	300	120	800	80	420~1260	×	比較例
20	0.4	1.5	0.2	2.1	300	40	550	60	100~460	×	比較例

[0023] From this result, it can consider as follows. First, it is the example with which are satisfied of the requirements specified by this invention, and, as for the thing of No.1-10, it turns out that the good appearance which does not have un-galvanizing in which conditions is acquired.

[0024] On the other hand, the thing of No.11-20 was an example of a comparison lacking in either of the requirements specified by this invention, and un-galvanizing had occurred and it was able to acquire the good appearance for neither. That is, as for the thing of No.11, Si content in a steel plate was over 2%, and the sum total content of Si, Mn, and Cr was over 5%, and even if the thing of No.12 had satisfied the oxidation reduction conditions specified by this invention, it was not able to acquire a good appearance.

[0025] moreover, reduction time amount (S2) the thing of No.14 which has oxidation time amount (S1) short [ the thing of No.13 ] [ long ] The thing of No.16 which has whenever [ oxidation board temperature / low / the thing of No.15 ] with high reduction hot-plate temperature The thing of No.20 which has oxidation time amount (S1) long [ the thing of No.19 which has whenever / high / the thing of No.18 which has reduction time amount (S2) short / No.17 / oxidation board temperature ] was not able to show each case where reduced temperature was low, and was not able to acquire a good appearance in which conditions.

[0026]

[Effect of the Invention] the front face at the time of annealing of elements, such as Si, Mn, Cr, etc. which are added by the steel plate by constituting this invention as mentioned above and making proper relation between oxidation conditions and reduction conditions, -- the hot-dip zinc-coated carbon steel sheet and alloying hot-

dip zinc-coated carbon steel sheet which have the good plating appearance which controls concentration and does not have un-galvanizing were obtained.

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[Translation done.]